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14. ABSTRACT The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.						
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# **POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE**

## ***Progress Report #2***

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### 1 Summary

Initial experiments with the handheld fluorescence microscope were successful in imaging Nile Red-loaded microcapsules within the self-healing paint. However, the microcapsule shells were brighter than the entrained fluid, making it difficult to assess the health of the coating. Shear strength measurements have commenced using a custom-built Couette viscometer. The microcapsule strength currently exceeds the maximum shear stress applied by the viscometer.

### 2 Project Goals and Objectives

The four milestones for phase IV are as follows:

1. Develop on site inspection method for monitoring self-healing and coating health by month 3.
2. Develop a method for continuous monitoring of OTS degradation by month 5.
3. Demonstrate a method for measuring the fraction of broken microcapsules as a function of shear stress by month 6.
4. Establish baseline metrics for qualifying batches of microcapsules from the manufacturing process by month 12.

### 3 Key Accomplishments

#### 3.1 On Site Inspection of Coating Health

Given the increased emphasis on field-testing in this program, a need has arisen to develop a reliable method for on site inspection. In order to understand the failure or success of a given test, it is crucial to somehow evaluate whether self-healing is occurring. The current method involves electrochemical impedance spectroscopy, but this method requires extensive equipment that may be impractical for certain test sites.

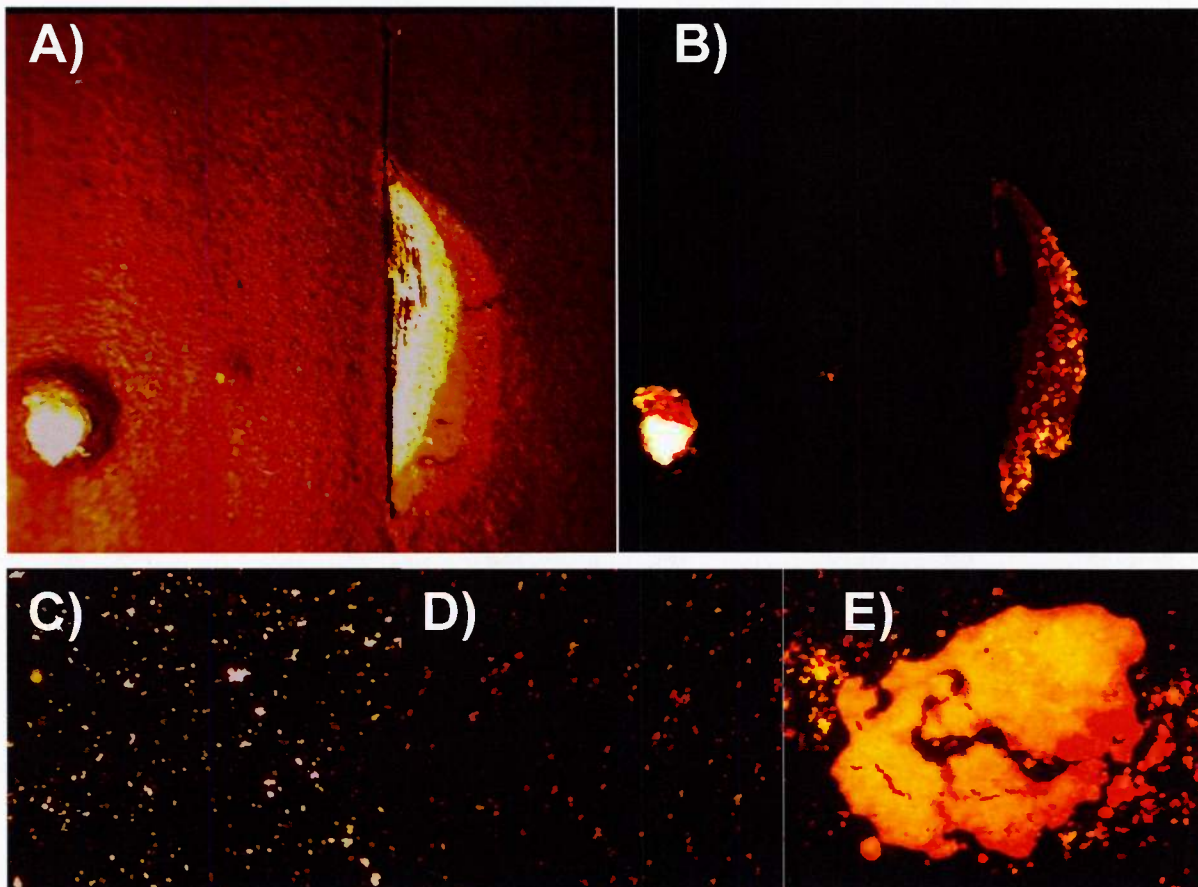


We have proposed the idea of imaging the red fluorescence of the Nile Red tracer dye that is incorporated into every microcapsule. The small handheld fluorescence microscope shown in Figure 1 connects to a laptop computer. Magnifications up to 200x reveal whether the silane spread uniformly across the scratch, or whether healing was incomplete.

Coating health is difficult to ascertain from on site measurements, but the handheld fluorescence microscope can also reveal whether uncured silane remains embedded within the self-healing paint. Here the coating will be gouged in select locations to look for evidence of liquid flowing from the cleaved microcapsules.



**Figure 1.** Dino-Lite handheld fluorescence microscope with Nile Red filter.



**Figure 2.** Microscopy images taken with handheld microscope. A) 200x image of a scratch and gouge in white light. B) The same in fluorescence imaging. C) Filled microcapsules appear only slightly brighter than D) empty microcapsules. E) The liquid corona surrounding a clump of broken microcapsules appears less bright than the broken shells in the center of the clump.

Figure 2A shows a gouge and scratch under white light illumination, whereas Figure 2B is filtered to reveal only the fluorescence. The microscope clearly shows the locations of microcapsules within the gouge, but it is not sensitive enough to image the liquid within the hairline scratch. Control samples were completely black in fluorescence mode for comparison.

Subsequent testing showed no change in fluorescence even when the broken microcapsules were washed with acetone and toluene. The observed fluorescence, therefore, is coming from the microcapsule shells. Nile Red is apparently partitioning strongly into the polymer shell. The bottom row of Figure 2 shows the small difference in brightness between C) filled and D) unfilled microcapsules. Even when the microcapsules are crushed beneath a cover slip, the liquid corona surrounding the microcapsules is actually less bright than the clumps of broken polymer shells in the center (Figure 2E).

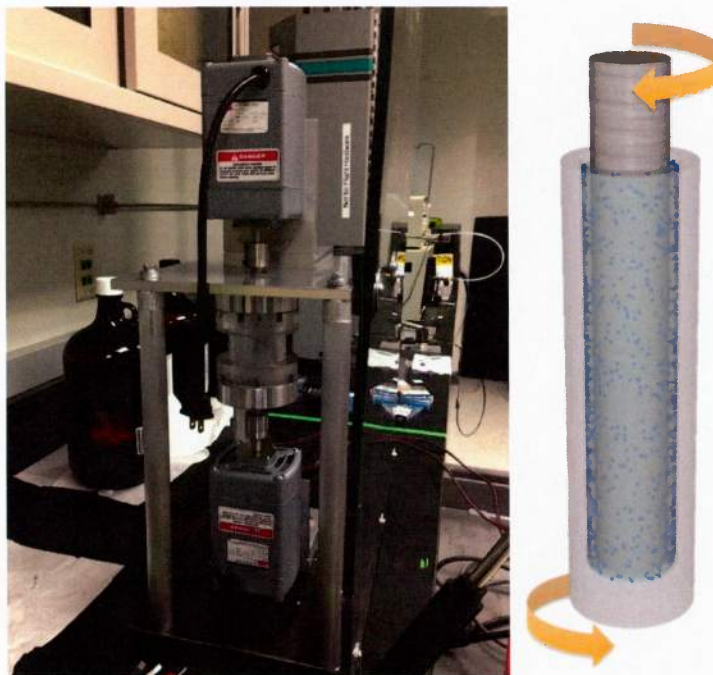
These early experiments demonstrate the value of the fluorescence microscope hardware, but they indicate that a different tracer dye may improve the utility of this inspection method. Specifically, a more hydrophobic fluorescent dye that partitions more strongly into the OTS will make it easier to evaluate whether the microcapsules retain liquid OTS and perhaps even determine whether that OTS is wicking across the scratch.

### 3.2 Microcapsule Shear Strength

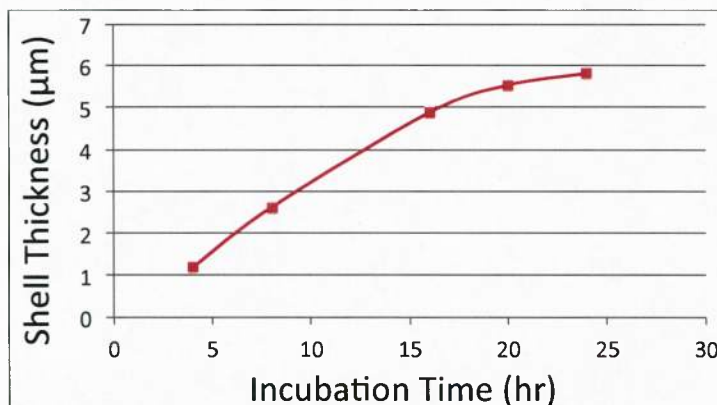
Before the paint is applied to a surface, the microcapsules undergo shear during filtration, paint mixing, and spraying. Since OTS is used as a mold release agent, one can imagine that premature rupture may cause unwanted adhesion problems. The shear strength should therefore be as high as possible. Being too strong does not appear to be a problem. Experience has shown that the microcapsules always fail when the coating fails. Moreover, their adhesion with the MIL-P-26915 zinc rich primer appears to be greater than their cohesive strength. We have never observed a case where microcapsules survived within a scratch by delaminating from the primer.

One of our goals in phase IV is to measure the fraction of broken microcapsules as a function of applied shear stress. We have therefore fabricated a custom Couette Viscometer to apply a known shear stress through fluid flow. The Couette Viscometer is shown in Figure 3. It has a maximum speed of 12000 RPM, the fluid has a 35 cSt viscosity, the outer inner diameter is 51 mm, and the inner outer diameter is 44 mm, giving a 7 mm gap.

The microcapsules made by the standard recipe do not break under even the maximum settings. While this is a positive development from a technology standpoint, it is still preferable to be able to quantify the shear strength by eventually noting the stress at which they fail. We have therefore endeavored to intentionally synthesize weaker microcapsules with thinner polymer shells to assist with metrology development. We tested three batches in all, with incubation times of 8, 16, and 24 hr at 90°C. The corresponding shell thickness is given in Figure 4. The 8 hr batch with 2.6  $\mu\text{m}$  shells breaks at 10000 RPM, but only a small fraction. More detailed data analysis is still underway.



**Figure 3.** The Couette viscometer consists of a pair of nested cylinders with a small gap. The cylinders rotate in opposite directions and generate a well-defined shear flow for the liquid within the gap.



**Figure 3.** Microcapsule shell thickness plotted as a function of incubation time at 90°C. The shell-forming IPDI is almost completely consumed after 24 hr, which is why the thickness plateaus around 6 μm.

### 3.3 Next Steps

We will continue to evaluate the kinetics of OTS hydrolysis within the microcapsules at elevated temperatures. We will explore alternative tracer dyes that might improve our ability to identify broken, solidified, or in tact microcapsules using fluorescence imaging. We will attempt to validate the shear strength test by increasing the applied shear stress and by decreasing the shear strength of the microcapsules. We will also begin to explore the self-healing mechanisms of surfaces exposed directly to OTS and other silanes.